UNIVERSITY OF PÉCS FACULTY OF SCIENCES INSTITUTE OF CHEMISTRY

STUDY OF 2,5-DI-TERT-BUTYL-1,4-BENZOQUINONE IN DIFFERENT SOLVENT MIXTURES: PHOTOCHEMICAL AND REDOX PROPERTIES



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Introduction

Nowadays, the world requires a tremendous amount of energy for industrial and everyday use. Energy comes in several ways, some of them are from the utilization of substances, and the others come from renewable sources. Since the demand for power increases every day, it is an advantage to use an energy source that would not cause any damage to the living organisms in the utilization area and nature in general. One way of getting energy in an ecofriendly way is the collect it from sunlight and store it for further use.

Our goal is to perform photochemical water splitting in a homogeneous aqueous medium using photo-catalysts and photo-sensitive molecules such as Ce(III) salts or 1,4-benzoquinones. The kinetics of the reactions is followed by spectrophotometry, which also provides the light source for the photoreaction.

A possible way to utilize solar energy is to use photochemical reactions oxidizing water (preferably in an aqueous medium); then, the reduced reaction partner can be used directly or indirectly to produce energy. One possible way is to use quinones as photosensitive compounds. Quinones are biological pigments that have been found in living organisms such as bacteria, fungi, higher plants, and other animals (Devi and Mehendale 2014). They exist in various forms, such as anthraquinones, polycyclic quinones, benzoquinones, and naphthoquinones. Quinones are, depending on their side chains, readily soluble in water. They can also be found in biological systems (*e.g.*, plastoquinones, photosystem II). When exposed to light, two major reaction types occur in their solutions: one gives hydroquinone and hydroxy-quinone, and the other has hydroquinone and oxygen as products. By altering the side chain, the redox properties of the resulting hydroquinone can also be changed.

1. Literature background

Hydroquinones, depending on their substituents, are sensitive to oxygen in a basic medium, which is a side reaction. Still, in addition to the reaction that reproduces the original quinone, it only decreases the efficiency of the desirable photoreaction without losing the quinone as the catalyst. The quinone-hydroquinone conversion can be useful and essential for flow batteries used in aqueous solutions of anthraquinones. As shown experimentally, this reaction is strongly influenced by light, so it is easy to increase the efficiency of a quinone-based flow battery with appropriate illumination or even fill the cell with light, *i.e.*, to convert solar energy into electrical energy.

$$1/2 \quad \bigcup_{OH}^{OH} + 1/2 \quad \bigcup_{OH}^{R} + 1/2 \quad \bigcup_{H_2O}^{H} \quad \bigoplus_{H_2O}^{H} \quad \bigoplus_{H_2O}^{R} \quad \bigoplus_{OH}^{Hv} + 1/2 O_2$$

Figure 1. p-Benzoquinone reaction with water in presence of UV light.

In my research project, the compound I planned to use is 2,5-di-tert-butyl-*p*-benzoquinone, which is not readily soluble in water but can be dissolved in some organic solvents. It would be preferable to use solvent mixtures containing water since water is one of the reactants of the photoreaction.



Figure 2. Structure of 2,5-di-tert-butyl-p-benzoquinone.

Since water is not a solvent, we can substitute it with organic solvents. However, one of the main goals is maintaining the solution's safety limits of organic solvent content. The answer to this problem can be mixing with water and not diluting it more than a 1:4 ratio of organic solvent to water; other proportions can also be assessed.

The kinetics of the photoreaction can be studied in a diode array spectrophotometer. A method is worked out that uses a diode array spectrophotometer as a photoreactor and analyzing unit simultaneously to carry out these measurements. This method uses a unique property of the diode array spectrophotometers, namely the high light intensity passing through the sample. This polychromatic UV-Vis light can induce photoreactions. The instrument, at the same time – being a spectrophotometer – can follow the kinetics of all reactions in the cell, accompanied by the change of color. In the absence of intense irradiation, a double beam spectrophotometer is used to study the reactions.

1.1 Redox Properties benzoquinone. Flow batteries.

Due to the increasingly high energy demand in developing and developed countries, original grid power sources cannot always serve optimally, and methods of electrical energy storage are needed. Meanwhile, environmental standards must also be met. Besides safe generation, optimal usage should also be considered.

One of the most recent technologies and a good choice is the redox flow battery (Ponce de León et al. 2006). The flow battery is the electrochemical cell that contains two tanks containing liquids. Substances provide power due to electrochemical processes proceeding in the cell. The reduction half-reaction at one electrode extracts electrons from one electrolyte, while the oxidation half-reaction at the other electrode recombines them into the additional electrolyte. Some ions also move between the electrolytes simultaneously.



Figure 3. Principe of a redox flow battery (M2N and Eindhoven).

Nowadays, along with inorganic cells, organic cells are developed by electrochemists. These cells perfectly operate with 4,5-dihydroxybenzene-1,3-disulfonic acid at the anode and anthraquinone-2,6-disulfonic acid at the cathode (Yang et al. 2016). Processes that happen in the battery are shown in Figures 4 and 5.



Figure 4. Schematic of the reaction principle of Organic Redox Flow Battery (ORBAT) using aqueous solutions of 4,5-dihydroxy-1,3-disulfonic acid (BQDS) on the anode (Yang et al. 2016).



Figure 5. Schematic of the reaction principle of Organic Redox Flow Battery (ORBAT) using an aqueous solution of anthraquinone-2,6-disulfonic acid (AQDS) on the cathode (Yang et al. 2016).

Benzoquinone derivatives were examined instead of anthraquinones in the redox flow battery system. A research group analyzed the redox couple of the hydroquinone-benzoquinone couple for electron transfer detection (Petrangolini, Alessandrini and Facci 2013). Based on the results of the research group of Dr. Zhenjing Yang and colleagues, the anthraquinone-based reactants, in comparison to benzoquinones, have higher alkaline solubility, lower molecular weight, and lower cost. However, there might be some enhanced membrane permeability due to lower molecular weight, thereby posing challenges for membrane development toward low molecular permeability while maintaining high ionic conductivity to prevent capacity fade due to molecular crossover. Fortunately, most of the membranes are stable up to pH 14. Substituted derivatives of dihydroxybenzoquinone substantially altered the capacity retention rate, solubility, and redox activity. Based on the results, also using computational screening in conjunction with these experiments, the research group pointed out

further performance improvements and potential opportunities for using benzoquinone-based alkaline organic redox flow batteries to provide safe, cost-effective, stationary electrical energy storage (Yang et al. 2018). Recently a research group base group in Harvard college, Cambridge proved that all-quinone/hydroxyquinone systems provide a path to very inexpensive stationary systems. Their research was considering p-benzoquinone/hydroquinone system (Nawar, Huskinson and Aziz 2012).

1.2 Photochemistry of benzoquinone

The UV spectrum of a 1,4-benzoquinone has three absorption bands depending on the transition of electrons in an aqueous solution. However, the wavelength of these transitions depends on the substitution of the quinone ring and solvent used. Upon the action of light in an aqueous solution, there is a color change of the solution to brown from the initial yellow. In earlier centuries, researchers believed this occurred due to the formation of a previously unknown substance in the solution, which was deemed a quinol (Hartley and Leonard 1909). Over the time, researchers had developed better instrumentation, and more precise detection was made:



Figure 6. Products of the photochemistry of p-benzoquinone in an aqueous solution (Ononye, McIntosh and Bolton 1986).

The initial steps of the photochemistry of the unsubstituted 1,4-benzoquinone were not known in sufficient depth. The photoreaction of an aqueous solution of benzoquinone can go in several pathways: 1) via semiquinone radical; 2) via water addition to the triplet state that has a lifetime less than 0.5µs with the intermediacy 1,2,4-trihydroxybenzenes (THBs). Since the concentration of benzoquinone plays a significant role in the determination of kinetic pathways, the last path is suitable at a low concentration of benzoquinones that does not form any radicals except in the last step, where THB reacts with the quinone (via non-observable radicals). Regardless of the steps, the photoreaction leads to equal amounts of hydroquinone and 2-hydroxy-*p*-benzoquinone, identical in both paths (Görner and von Sonntag 2008). However, in the primary step of the photochemical reaction, many groups postulated that free hydroxide radicals formed from water (Ononye et al. 1986, Pochon et al. 2002, Alegría, Ferrer and Sepúlveda 1997).

1.3 Reaction of benzoquinone derivatives with hydrogen peroxide

The reaction between benzoquinone and hydrogen peroxide occurs with hydroxybenzoquinone production and follows the reaction scheme: Q – benzoquinone; QR – benzoquinone derivative (Józsa et al. 2014).

$$QR + H_2O_2 \rightarrow QR - O^- + H^+$$
(1)



Figure 7. Structural scheme of reaction (1).

The rate law confirms that it is first order with respect to both benzoquinone and hydrogen peroxide and inverse first order with respect to the hydrogen ion, which is interpreted by a rate-controlling reaction between the quinone and the mononegative hydroperoxide ion (Józsa et al. 2022).

$$r = k \times \frac{[QR] \times [H_2 O_2]}{[H^+]} = k_{\phi}[QR]$$
 (2)

The reaction should proceed only in an acidic medium due to the polymerization of hydroxy-1,4-benzoquinones in a basic medium (Kurien and Robins 1970). Since the concentration of the hydrogen peroxide is much higher than benzoquinone and the concentration of the hydrogen ion is stabilized by buffer solution, a pseudo-first-order rate constant (k_{ϕ}) is introduced to the equation.

We ensured a nucleophilic attack of hydroperoxide ion (HO₂⁻) during the reaction on the benzoquinone ring, which is a rate-determining step of the reaction. However, this attack occurs only on hydrogen-containing carbon of the ring (Józsa et al. 2022). The oxidizing properties of deprotonated hydrogen peroxide (Lente and Espenson 2004) can be explained by the following dissociation:

$$H_2O_2 \rightleftharpoons HO_2^- + H^+ \qquad \qquad K_a = \frac{[HO_2^-] \times [H^+]}{[H_2O_2]}$$
(3)

The rate-determining reaction would seem this way:

$$QR + HO_2^- \xrightarrow{\kappa_r} QR - OH + OH^-$$
(4)

rate constant:
$$k_{\rm r} = \frac{k}{K_a}$$
 (5)

1.4 Spectrophotometer as a photoreactor

Spectrophotometry is one of the most widely used methods in chemistry. Due to its simplicity, reliability, and low-cost, it is commonly used for both direct measurements and coupled to other techniques or processes such as chromatography, electrophoresis, and flow analysis (Rocha and Teixeira 2004).

A spectrophotometer is a device that measures absorbance at different wavelength ranges, usually between 190 and 1100 nm; with continuous illumination, it can measure throughout the given time. The light source of a diode-array spectrophotometer usually contains a deuterium and halogen lamp. The result shows an amount of measured transmitted light as a function of wavelength. Measured absorbance can be used for quantitative analysis due to the Lamber-Beer law and determining reaction kinetics. However, spectrophotometers can cause unexpected phenomena in photosensitive systems, as they can induce photochemical reactions by absorbing light. These processes must be considered; otherwise, we may get a false result. Despite this, it allows us to measure the kinetics of photoreactions. Since light is induced toward the sample, it should be placed into an appropriately covered vessel or cell: we used a 1.00 cm cuvette of quartz. However, it should be ensured that there would be no primary reactions on the side of induction since the not whole sample is illuminated. A spectrophotometer can be used as a photoreactor. Two Hungarian chemists, namely Dr. Gábor Lente and Dr. István Fábián, proved that the spectrophotometer is excellently fitted to the requirements of a photoreactor (Fabian and Lente 2010).

2. Experimental methods

2.1 Reagents used

Solid compound benzoquinone and its derivatives were provided by Sigma Aldrich. For the measurements, solutions of 2,5-di-tert-butyl-p-benzoquinone with 0.02 mol/dm³, 0.01 mol/dm³, 0.0001 mol/dm³ concentrations were prepared and analyzed. Water, DMSO, 2-propanol, acetonitrile, and acetone were tested as solvents. Due to the low solubility of the compound in water and 2-propanol, the sample was stirred for 5 minutes for 2-propanol and twice by half an hour for water using an EMMY-40-HC-EMAG ultrasonic bath at room temperature. Due to the photosensitivity of the benzoquinone derivative solution, the were stored in a dark place, thus minimizing contact with light. No significant change was detected after storing up to seven days. Thus, the date of preparation was signed on each flask containing the solution; after seven days, a new solution was prepared.

30 m/m% hydrogen peroxide solution was used as the stock solution manufactured by VWR International byba Geldenaaksebaan 464-B-300| Leuven Belgium. Due to the measurable decomposition of H₂O₂, the stock solution was stored in a fridge, and small portions were used for measuring reaction kinetics.

Some experiments were performed in a buffered medium with phosphate buffer (p K_{a2} = 7.20). 1.00 mol/dm³ aqueous solution from solid NaH₂PO₄·2H₂O and Na₂HPO₄·2H₂O was prepared.

2.2 Measurement methods

Analysis of the measurements is one of the essential parts of research. Stock solutions prepared must be analyzed using a spectrophotometer SPECORD-600 and collected results filtered and observed numerically and graphically by Microsoft Excel. The kinetic curve was evaluated using the initial rate method.

The accuracy of the results obtained should also be studied using SciDAVis (*Scientific Data Analysis and Visualization*) software. Several parameters describe the accuracy of the results: standard deviation of both slope and intercept, R² variance of the predicted values divided by the variance of the data (Gelman et al. 2019), Chi² is used to verify the null

hypothesis H(0), which assumes that there is no significant difference between expected and observed data (Kwasiborski and Sobol 2011).

2.3 UV-visible spectrophotometry

Kinetic measurements of benzoquinone were performed by the UV-visible spectrophotometry at 23 ± 1 °C. The spectra obtained from WinASPECT were recorded with a software-controlled AJ SP S600 diode-array spectrophotometer. The spectra were recorded at 180-1100 nm. However, in the evaluation, it was sufficient to consider the spectral range from 180 to 600 nm. The cuvette was made from quartz with a path length of 1.00 cm and mixed with a stirrer built into the cuvette holder.

3. Results and discussion

Compared with other quinones, 2,5-di-tert-butyl-p-benzoquinone is sparingly soluble in water. Different solvents were examined.

Comparing other solvents, we took dimethyl sulfoxide, pure propanol, acetonitrile, and acetone. Only water and dimethyl sulfoxide could not dissolve the given compound, while others turned to yellow after dissolution. Since we had to consider the water toleration of the solution, we had to test this property. Water toleration was checked by adding a drop of water into each solution to avoid dramatic changes.

Water	Isopropanol +	Acetone +	Acetonitrile +	Acetonitrile +
drops	compound	compound	compound (not fresh)	compound (fresh)
1	No change	No change	No change	No change
2	No change	No change	No change	No change
3	No change No change		No change	No change
4	No change	Starts blurring	No change	No change
5	No change	Blurry solution	No change	No change
6	No change	Blurry solution	No change	No change
7	No change	o change Blurry solution Blurry solution		Blurry solution
8	No change	Blurry solution	Blurry solution	Blurry solution

 Table 1. Water toleration of different solvents.

Minor gases were present while shaking the solution after adding water droplets. New and old acetonitrile solutions were prepared in 2 days apart and examined. The old solution of benzoquinone derivative in acetonitrile had an orange color while fresh had yellow color. Summarizing all the results, we had to proceed with.

For analyzing the absorbance 0.01 M, 0.02 M, 0.0001 M, 0.00001 M solutions of 2,5di-tert-butyl-*p*-benzoquinone in isopropanol had been prepared. Before the absorbance measurement, we tested whether the solvent itself absorbs light. The absorbance of the solvent was measured for 30 minutes to yield information about the stability.



Figure 8. Measurement of the solvent spectrum (2-propanol) for 30 mins in a diode array spectrophotometer.

Absorption of 0.01 M solution was measured for 60 minutes and indicated a decrease in absorption of about 0.005 units overall at 451.5 nm.





Figure 9. Kinetic curve of 0.01M solution of 2,5-di-tert-butyl-p-benzoquinone in 2-propanol at 451.5 nm for 60 mins.



Also, 0.01 M solution was measured for 30 minutes to observe any differences in the absorption at 451.5 nm.

From x = 0 to $x = 1\ 800$ B (y-intercept) = 0,255 \pm 0,00028 A (slope) = -2,92e-06 \pm 2,68e-07 Chi^2 = 1,86e-05

Figure 10. Kinetic curve of 0.01 M solution of 2,5-di-tert-butyl-*p*-benzoquinone in 2-propanol at 451.5 nm for 30 mins.

As we can see that there is a change between the two periods. So, it means that absorption decrease changes over time; the more time we wait, the smaller decrease we see. To see how absorption changes at more dilute solutions, 0.0001 M and 0.00001 M solutions were measured at the same wavelength for 30 minutes.



From x = 0 to $x = 1\,800$ B (y-intercept) = 0,0249 ± 8,25e-05 A (slope) = -1,12e-06 ± 7,93e-08 Chi^2 = 5,56e-05

Figure 11. Kinetic curve of 0.0001 M solution of 2,5-di-tert-butyl-*p*-benzoquinone in 2-propanol at 451.5 nm for 30 mins.



From x = 0 to $x = 1\,800$ B (y-intercept) = 0,00216 ± 8,4e-05 A (slope) = -8,165e-07 ± 8,07e-08 Chi^2 = 5,76e-05





However, we also checked their absorbance difference at their maximum wavelength of 0.0001 M and 0.00001 M.

 $From \ x = 0 \ to \ x = 1 \ 800$ B (y-intercept) = 0,3 ± 0,00028 A (slope) = 6,62e-05 ± 2,7e-07 Chi^2 = 0,00065

Figure 13. Kinetic curve of 0.0001M solution of 2,5-di-tert-butyl-p-benzoquinone in 2-propanol at 298.5 nm for 30 mins.



From x = 0 to $x = 1\,800$ B (y-intercept) = 0,035 ± 0,00012 A (slope) = 2,52e-05 ± 1,19e-07 Chi^2 = 0,000125

Figure 14. Kinetic curve of 0.00001M solution of 2,5-di-tert-butyl-p-benzoquinone in 2-propanol at 294.5 nm for 30 mins.

Even though they show a decrease in absorbance at 451.5 nm, they also demonstrate an increase in absorbance at 298.5 and 294.5 nm. However, along with this, we can see that the dilution absorbance slope changes 2.33 times.

Upon measurement, it was decided to prepare a solution of 0.02 M to see if it would have more absorbance. It yielded the following results:



 $From \ x = 0 \ to \ x = 3 \ 600 \\ B \ (y-intercept) = 0.577 \pm 0.00028 \\ A \ (slope) = -1.26e-06 \pm 1.337e-07 \\ Chi^2 = 7.18e-05 \\ \end{cases}$



However, it showed the same decrease in absorbance as a solvent.



From
$$x = 0$$
 to $x = 1\ 800$
B (y-intercept) = 0.58 ± 0.00054
A (slope) = $-2.45e-06 \pm 5.18e-07$
Chi^2 = $6.962e-05$

Figure 16. Kinetic curve of 0.02M solution of 2,5-di-tert-butyl-p-benzoquinone in 2-propanol at 451.5 nm for 30 mins.

It demonstrates a twice lower decrease in absorption than 60 min, which means that the solution starts to gain absorption for a longer time rather than lose it.

To see some reaction abilities of our solution, we started to prepare a buffer solution from dihydrogen phosphate and hydrogen phosphate mixture with a 1:1 proportion to reach 1.00 M of each in a 100 cm³ volumetric flask. The buffer solution was prepared to maintain pH around neutral and observe the absorbance difference of the solution under these conditions.

The following figure shows the results:



Figure 17. Absorbance curve of 1M solution of H₂PO₄^{-/}HPO₄²⁻ buffer with 0.02M solution of 2,5-di-tertbutyl-p-benzoquinone in 2-propanol at different wavelengths for 30 mins.

The results were surprisingly more or less stable at each wavelength since the beginning of the measurement. Meanwhile, the solution produced a residue, which led us to measure water toleration by containing 2,5-di-tert-butyl-benzoquinone.

Buffer/solution	0.02 M	0.01 M	0.0001 M	0.00001 M
proportions	solution	solution	solution	solution
1:1	Precipitate ↓	Precipitate ↓	Precipitate ↓	Precipitate ↓
1:2	Precipitate ↓	Precipitate ↓	Precipitate ↓	Precipitate ↓
1:3	Precipitate ↓	Precipitate ↓	Precipitate ↓	Precipitate ↓
1:4	Precipitate ↓	Precipitate ↓	Precipitate ↓	Precipitate ↓
1:50	Precipitate ↓	Precipitate ↓	Precipitate ↓	Precipitate ↓
1:99	No change	Precipitate ↓	Precipitate ↓	Precipitate ↓

 Table 2. Buffer toleration of the solution of different concentrations.

Since all proportions perform precipitation in Table 2, the only ratio which did not indicate any change was 0.02 M of the solution to the buffer is a 99:1 proportion. The absorbance of these conditions was measured.



Figure 18. Absorbance curve of 1M solution of H₂PO₄⁻/HPO₄²⁻ buffer with 0.02M solution of 2,5-di-tertbutyl-*p*-benzoquinone in 2-propanol with proportion 1:99 at different wavelengths.

As we can see, by the time absorbance of this mixture decreases, we can compare the absorbance value initial and after 3600 seconds. At 451.5 nm, they indicate the following results:



From x = 0 to $x = 3\ 600$ B (y-intercept) = 0,35 ± 0,00043 A (slope) = -6,27e-06 ± 2,07e-07 Chi^2 = 0,000176

Figure 18. Kinetic curve of 1M solution of H₂PO₄⁻/HPO₄²⁻ buffer with 0.02 M solution of 2,5-di-tert-butyl*p*-benzoquinone in 2-propanol with proportion 1:99 at 451.5 nm for 1 hour.

Summarizing a linear equation, a negative slope indicates a nondramatic decrease in absorbance. However, some small precipitate particles were detected after measurement. Due to the decreasing amount of substance, the absorbance of the solution mixture was also decreasing.

Since the main goal is to check whether the solution reacts with hydrogen peroxide and borax, the absorbance of the reaction between hydrogen peroxide and 0.02 M solution was measured. However, the exact proportions of hydrogen peroxide to 0.02 M solution precipitation were detected initially. That is why other ratios such as 1:3 and 1:5 were examined, which surprisingly dissolved the precipitate while adding an excess amount of solution and constant stirring.

Examination of 1:3 proportion at 451.5 nm:



 $From x = 0 \text{ to } x = 1\ 800$ B (y-intercept) = 0,46 ± 0,0003 A (slope) = -8,097e-06 ± 2,95e-07 Chi^2 = 2,25e-05

Figure 19. Kinetic curve of 30% hydrogen peroxide solution with 0.02M solution of 2,5-di-tert-butyl-pbenzoquinone in 2-propanol with proportion 1:3 at 451.5 nm.

Examination of 1:5 proportion at 451.5 nm:



From x = 0 to x = 1 800 B (y-intercept) = 0,49 ± 0,00044 A (slope) = -5,251e-06 ± 4,215e-07 Chi^2 = 4,6e-05

Figure 20. Kinetic curve of 30% hydrogen peroxide solution with 0.02 M solution of 2,5-di-tert-butyl-*p*-benzoquinone in 2-propanol with proportion 1:5 at 451.5 nm.

Due to the absence of significant and negligible differences in absorbance throughout the whole time, we can be sure that no reaction occurs between the two substances.

4. Summary

We are now sure that various sources provide a tremendous amount of energy, such as solar, wind, hydropower, geothermal, and biomass. Several methods of converting light into energy use chemical reactions, such as flow batteries, bioelectrochemical, solar, and photocells. The research aims to determine the photochemical and redox properties of 1,4-benzoquinone derivatives in ecofriendly medium conditions.

In my dissertation, I chose 2,5-di-tert-butyl-1,4-benzoquinone as a derivative compound to be analyzed since no one has observed it until now. However, due to the lack of solubility of the 1,4-benzoquinones and especially 2-tert-butyl-1,4-benzoquinone, the 2,5-di-tert-butyl-1,4-benzoquinone did not excel. Among all available solvents, 2-propanol was chosen as a solvent. A photoreaction with the hydrogen peroxide did not change the absorption spectra, but the precipitation in the reaction vessel was detected in an unsuitable proportion. Different proportions were measured; only by increasing the volume did precipitation formation significantly decrease. The initial aim of using 20% of 2-propanol in water as a solvent mixture was not reached because of our compound's sensitivity to water. Examining 2-propanol-based solution with buffer solution, no change in absorption spectra was detected, but the precipitate formation was detected.

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7. Declaration

DECLARATION

of the originality of the writing

(According to Code of Studies and Examinations of the University of Pécs, Annex nr. 14/1.)

I, the undersigned, **Nurzhan Tursyn**, **GU00Z9** (NEPTUN system identifier), declare under penalty of perjury that every part of my writing, including the scientific conclusions, graphs, and codes shown in this thesis, is the result of my own, autonomous work, I only used referred sources (special literature, tools, etc.) and I observed the pertaining rules of the University of Pécs while preparing my writing.

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